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## Preparation of Cellobiose Octa(n-alkanoate)s and Their Thermal Properties\*

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Cellobiose octa(n-alkanoate)s ( $C_n$ OA's) of varying acyl length were prepared, and their thermal and structural properties were studied by differential scanning calorimetry, polarization optical microscopy, and polarization infrared spectroscopy (PIR).  $C_n$ OA's with an acyl length between 6 and 14 in carbon number were found to form a thermotropic liquid crystal. Comparison of their thermal data with those of cellulose tri(n-alkanoate)s indicated different structuring principles for the oligomer and polymer systems, consistently with the previous studies by X-ray diffraction. The PIR data were apparently consistent with the proposed discotic columnar structuring of  $C_n$ OA molecules.

KEY WORDS: Acyl cellobiose / Acyl cellulose / Calorimetry / Polarization FT/IR / Discotic columnar phase

### INTRODUCTION

Cellobiose, an oligosaccharide composed of two D-glucose units jointed by a 1, 4- $\beta$ -glycosidic bond, is the smallest compound possessing the structural characteristics of cellulose, which is a well-known source of a number of mainchain liquid crystals.<sup>1)</sup> Studies of such an oligomer and its derivatives are expected to provide key information for understanding the nature and origins of cellulosic liquid crystals.

Aside from this, cellobiose itself has been found to be a source of new interesting mesogens.<sup>2-4)</sup> For example, n-alkyl 1-O- $\beta$ -D-cellobiosides of appropriate alkyl length form a smectic-type phase that is believed to be stabilized mainly by hydrogen-bonding among glucopyranose rings stacked face by face. Their textures strongly suggest existence of a helical order in this phase.<sup>4)</sup> Cellobiose octa(n-decanoate), a fully acylated cellobiose, was observed to form a different type of thermotropic phase. An X-ray diffraction study has shown that this liquid crystal is classed as a discotic columnar phase, in which "columns" built up by a regular stacking of cellobiose "discs" are packed in a two-dimensional hexagonal order.<sup>2)</sup>

In this paper, we have prepared a series of cellobiose octa(n-alkanoate)s with varying alkyl length and studied their thermal properties by differential scanning calorimetry (DSC), polarizing optical microscopy, and polarizing infrared spectroscopy. The thermal data will be discussed in comparison with those for the polymer (cellulose) homologues.

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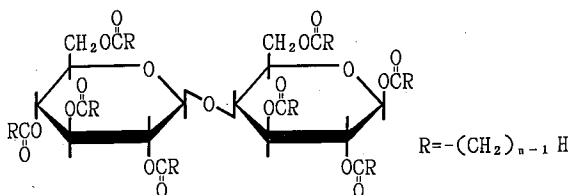
## EXPERIMENTAL

### Materials

D(+)-cellobiose (guaranteed grade) was obtained from Nacalai Tesque Inc., Kyoto and used as received. Deionized water was used throughout the experiments. All other chemicals were of reagent grade and used without further purification.

### Sample preparation

Cellobiose octa(n-alkanoate)s ( $C_bOA$ 's) were prepared by the acid chloride-pyridine procedure according to the method of Malm *et al*<sup>5)</sup>; to a suspension of cellobiose ( $3 \times 10^{-3}$  mol) in 20 ml of 1,4-dioxane, pyridine ( $3.4 \times 10^{-2}$  mol) and then an acid chloride ( $2 \times 10^{-2}$  mol) were added dropwise. The reaction was carried out under reflux for 18h. The reaction mixture was poured into a large excess of methanol-water (90 to 10 by volume) mixture, and the white precipitate was recovered by filtration and dried. This raw product was dissolved in tetrahydrofuran (THF) and centrifuged to remove insoluble materials. The sample was recovered by precipitation with hot methanol. This procedure was repeated until a sufficient purity was attained. Prepared  $C_bOA$  samples have the following general formula where the length of the ester side chain ranged from 6 to 14 in carbon number  $n$ . The sample will be designated by attaching  $n$  to the abbreviation, e.g.,  $C_bOA-10$  for cellobiose octa(n-decanoate).



### Determination of unreacted OH groups

To check possible existence of unreacted OH groups, an aliquot of each sample was treated with phenyl isocyanate in pyridine at 100°C. Excess phenyl isocyanate was removed by precipitating and washing the product in methanol. The amount of carbanilate introduced was estimated on the basis of the UV absorbance of the chloroform solution at 280 nm using a Shimadzu UV-200S spectrometer.

### Measurements

DSC measurements were made on a Rigaku-Denki Model DSC-8230, at a constant scanning rate of 10°C/min. Polarized optical microscopic observations were made with a Nikon Model Optiphot-Pol equipped with a Mettler hot stage Model FP-82 and a temperature controller Model FP-80. Infrared (IR) spectra were obtained with a JASCO FT/IR spectrometer Model 8800.

## RESULTS AND DISCUSSION

### Sample characterization

A cellobiose molecule carries eight OH groups, so that fully esterified derivatives should have a degree of substitution DS of 8. Three methods, IR and ultraviolet(UV) spectroscopies and elemental analysis, were used to determine the DS values of the prepared C<sub>6</sub>OA's. As an example, the IR spectrum of C<sub>6</sub>OA-10 is shown in Figure 1 together with that of cellobiose C<sub>6</sub> itself. The absorption bands observed for the ester at around 2,900 and 1,750 cm<sup>-1</sup> are due to the CH and C=O stretching vibrations, respectively. Complete esterification is confirmed by the almost entire absence of the large O—H absorption at around 3,400 cm<sup>-1</sup> observed for C<sub>6</sub>.

Table 1 shows the results of elemental analysis. The observed values well agree with those calculated for the corresponding cellobiose alkyl esters with a DS value of 8. The completeness of esterification was also checked by the UV measurements of the phenyl isocyanate-treated specimens. Because the phenyl carbanilation of the OH groups possibly remaining unreacted in a cellobiose moiety is expected to proceed

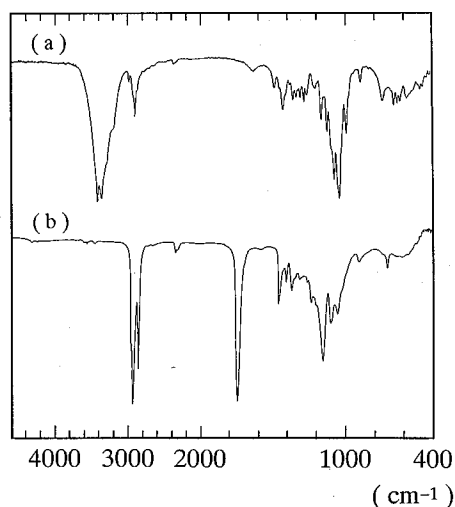


Fig. 1 FT/IR spectra of (a) C<sub>6</sub> and (b) C<sub>6</sub>OA-10.

Table 1 Results of Elemental Analysis

| n  | Calculated |       | Found |       |
|----|------------|-------|-------|-------|
|    | C(%)       | H(%)  | C(%)  | H(%)  |
| 6  | 63.92      | 9.12  | 63.77 | 9.07  |
| 7  | 65.88      | 9.59  | 65.84 | 9.64  |
| 8  | 67.52      | 9.99  | 67.04 | 9.90  |
| 9  | 68.91      | 10.33 | 68.78 | 10.37 |
| 10 | 70.10      | 10.61 | 70.02 | 10.63 |
| 12 | 72.04      | 11.08 | 71.69 | 11.01 |
| 14 | 73.54      | 11.45 | 73.31 | 11.28 |

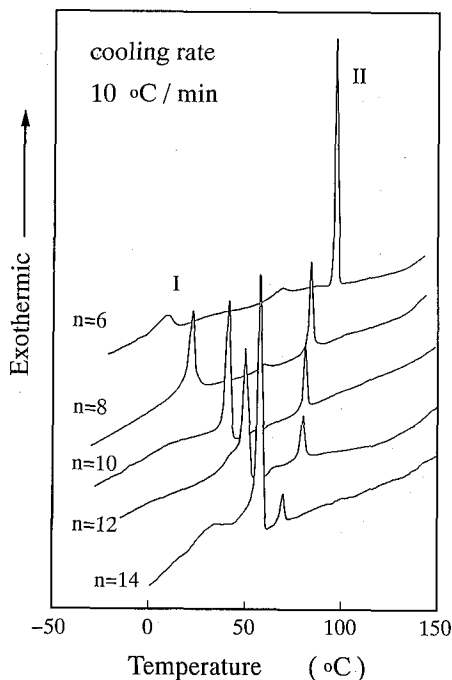


Fig. 2 DSC thermograms for  $C_bOA$ 's taken at a cooling rate of  $10^\circ\text{C}/\text{min}$ .

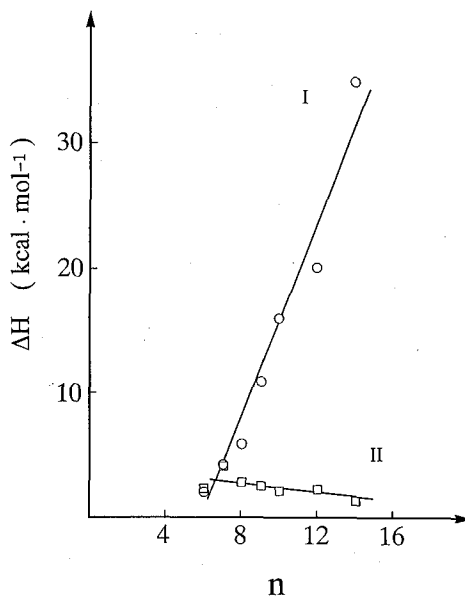


Fig. 3 Transition enthalpies of  $C_bOA$ 's as a function of acyl length  $n$ .

virtually perfectly, the degree of esterification can be deduced from the degree of phenyl carbanilation,  $DS_{PC}$ .  $DS_{PC}$  was estimated by use of a calibration curve established for the phenyl methylcarbanilate absorbance at 280 nm. In all cases, it was found that  $DS_{PC} \leq 0.03$ , namely practically complete esterification.

### Thermal properties of $C_bOA$ 's

Figure 2 shows the DSC thermograms of  $C_bOA$ 's observed in a cooling mode. All the derivatives studied ( $6 \leq n \leq 14$ ) have two exothermic peaks I and II (derivatives with  $n \leq 5$  or  $n \geq 15$  showed only one peak). Figure 3 shows the transition enthalpies  $\Delta H_I$  and  $\Delta H_{II}$  relevant to the two peaks.  $\Delta H_I$ , which sharply increases with  $n$ , may be attributed to the melting of the solid crystal. The slope of the line I in the figure gives a transition enthalpy of  $0.5 \text{ kcal/mol-CH}_2$ , i.e., *per methylene unit of the acyl group*. This is about half that for  $n$ -alkanes,<sup>7)</sup> and nearly the same as that for cellulose trialkanoates.<sup>6)</sup>

Peak II is associated with an isotropic-anisotropic phase transition. Photomicroscopic observation in fact confirms that at temperatures between peaks I and II, a liquid crystal is formed. Figure 4a shows the texture of the mesophase of  $C_bOA$ -10 formed by cooling it from the isotropic state. A mosaic or fan-shaped texture can be seen. Detailed textural observations along with an X-ray diffraction analysis have revealed that the phase is classed as a discotic columnar in type.<sup>2)</sup> Other  $C_bOA$ 's showed essentially similar textures to this, indicating that they all belong to the same type of liquid crystals.

The isotropization enthalpy  $\Delta H_{II}$  decreases with increasing acyl length  $n$ , ranging

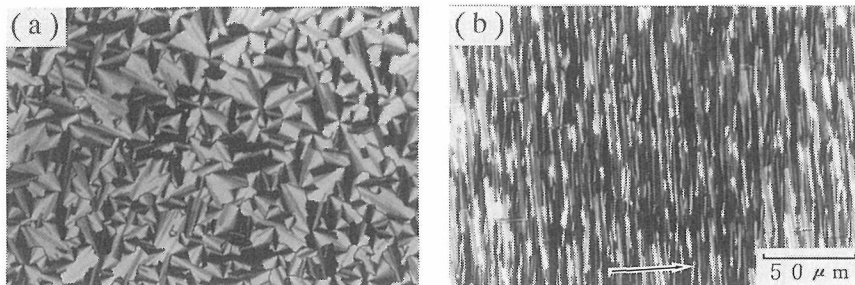


Fig. 4 Photomicrographs of  $C_6OA-10$ , (a) before and (b) after shearing; the arrowhead indicates the shearing direction.

from about 2.5 kcal/mol for  $n=6$  to about 1.3 kcal/mol for  $n=14$  (Figure 3). This probably indicates that  $\Delta H_{II}$  is associated mainly with the energetic interactions among glucopyranose "cores" rather than those among alkyl side-chain "fringes". If the latter interactions were important,  $\Delta H_{II}$  should increase with increasing  $n$ , just as  $\Delta H_I$  does. A decrease of isotropization enthalpy with increasing  $n$  was also observed for cellulose trialkanoates.<sup>6)</sup> However, their  $\Delta H_{II}$  values per glucopyranose unit were appreciably smaller than those of the cellobiose equivalents. This suggests different structuring principles for the cellulose and cellobiose systems. Even though they both are classed as a columnar in type,<sup>2,6)</sup> there is a distinct difference in their structures. In the cellobiose system, the "columns" are built up by a regular stacking of the cellobiose "discs", thus allowing close contacts of adjacent glucopyranose rings.<sup>2)</sup> In the cellulose system, on the other hand, the columnar and molecular axes parallel each other, and the two-dimensional hexagonal order of the columnar axes<sup>6)</sup> implies a difficulty for glucopyranose rings to contact each other so closely as in the cellobiose system.

The difference between the cellobiose and cellulose systems is also suggested in Figure 2, showing that the mesomorphic temperature region becomes narrower with increasing  $n$ . This contrasts to the behavior of the cellulose system, in which the mesomorphic region becomes wider with increasing  $n$  for  $n \leq 10$  and stays approximately constant for a further increase in  $n$ .<sup>6)</sup> Moreover, preliminary results indicate that the isotropization temperature of cellulose tridecanoate is an increasing function of degree of polymerization (DP),<sup>8)</sup> while that in the oligomeric system decreases with increasing DP, i.e., dimer > trimer > tetramer.<sup>9)</sup>

Another comment to be made in this connection concerns octa( $n$ -alkyl)- $\beta$ -D-cellobioside, a fully etherfied cellobiose. Interestingly, this compound forms no meso-phase for any alkyl length.<sup>10)</sup> It follows that carbonyl groups play an essential part in stabilizing the mesophase of the cellobiose esters.

### Polarization IR analysis

An attempt was made to observe the degree of orientation of carbonyl and other groups in the  $C_6OA$  mesophase by means of polarization IR spectroscopy. Figure 4b shows the texture of  $C_6OA-10$  (Figure 4a) after sheared by pressing and sliding the

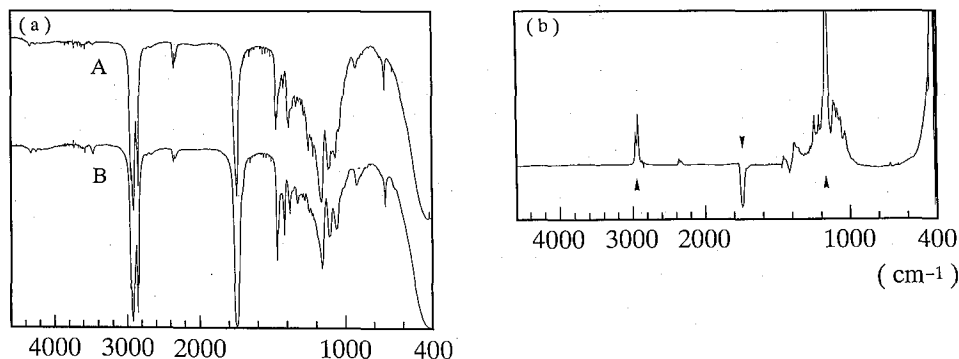


Fig. 5 (a) Polarized FT/IR spectra of  $C_6OA$ -10 with the polarizer perpendicular(A) and parallel(B) to the shear applied to the specimen; (b) An A-B difference spectrum.

specimen between microscopic cover glasses. Generally, the textures of  $C_6OA$ 's, once formed, are quite stable against temperature changes. Figure 5a shows the polarized IR spectra of the sheared  $C_6OA$ -10. The plane of polarization is either perpendicular (spectrum A) or parallel (spectrum B) to the shearing direction. The A-B difference spectrum given in Figure 5b shows two positive main peaks at around  $1200\text{ cm}^{-1}$  (ester C—O stretching) and around  $2900\text{ cm}^{-1}$  ( $CH_2$  stretching) and one negative main peak at around  $1750\text{ cm}^{-1}$  (C=O stretching). It is indicated that the C=O and C—O bonds are appreciably oriented parallelly and perpendicularly, respectively, to the shearing direction. The positive  $CH_2$  peak would imply that the alkyl C—H bonds are somewhat oriented along the shearing direction, or equivalently, the C—C bonds are oriented normally to the shear. These observations appear to be consistent with the discotic columnar structuring of  $C_6OA$  molecules,<sup>2)</sup> in which the more or less extended alkyl fringes protruding out from the columns of glucopyranose cores are believed to play an important part to stabilize the two-dimensional hexagonal ordering of the columns.

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